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SOLID OXIDE FUEL CELL BASED UPON COLLOIDAL DEPOSITION OF THIN FILMS FOR LOWER TEMPERATURE OPERATION (PREPRINT)

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14. ABSTRACT

In order to reduce the operating temperature of solid oxide fuel cells (SOFCs), anode-supported cells incorporating thin film (~ 10 μm) electrolytes in conjunction with anode/electrolyte and cathode/electrolyte interlayers were studied. SOFC button cells were prepared through deposition of colloidal slurries onto anode supported substrates and were analyzed as a junction of temperature and polarization via Voltammetry and Electrochemical Impedance Spectroscopy (EIS). Single SOFC button cells with electrode interlayers were then characterized as a junction of temperature and polarization to assess the involvement of these interfacial layers. EIS was applied and the data were used to deconvolute component impedances. Finally electrochemical models were developed to provide a more complete understanding of these assemblies under operation.

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Solid Oxide Fuel Cell Based Upon Colloidal Deposition of Thin Films for Lower Temperature Operation

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Abstract: *In order to reduce the operating temperature of solid oxide fuel cells (SOFCs), anode-supported cells incorporating thin film (~10 μm) electrolytes in conjunction with anode/electrolyte and cathode/electrolyte interlayers were studied. SOFC button cells were prepared through deposition of colloidal slurries onto anode supported substrates and were analyzed as a function of temperature and polarization via Voltammetry and Electrochemical Impedance Spectroscopy (EIS). Single SOFC button cells with electrode interlayers were then characterized as a function of temperature and polarization to assess the involvement of these interfacial layers. EIS was applied and the data were used to deconvolute component impedances. Finally electrochemical models were developed to provide a more complete understanding of these assemblies under operation.*

Keywords: SOFCs; fuel cells; thin films; EIS

Introduction

Solid oxide fuel cells (SOFCs) are energy conversion devices that produce electricity by electrochemically combining reactions of fuel and oxidant gases across an ionic-conducting ceramic. SOFCs are expected to be become very competitive devices for electrical power generation because of their high efficiency and reduced pollution operation. In conventional SOFCs, the electrolyte is yttria-stabilized zirconia (YSZ) with thickness of ~200 μm, and the operating temperature is around 900-1000°C. Such high operation temperatures of conventional SOFCs places considerable constraints on materials which can be used for interconnections and construction. Lowering the operation temperature is very important for making SOFCs cost effective. However, with lower operating temperatures, resistive losses across the electrolyte increase, overpotentials at electrodes are magnified and therefore the performance of the cell decreases. The present work seeks to find a solution for this problem by examining low temperature, high power density SOFCs employing thin-film electrolytes and interlayers. The objective of this effort was to characterize the anode and cathode performance enhancement of thin film, anode-supported SOFCs

when anode and cathode interlayers are included between the electrode and electrolyte interface. SOFC button cells containing the interlayers were evaluated as a function of temperature and polarization. EIS was used to generate a more complete understanding of how these interfaces improve cell performance. Finally, models were prepared based upon polarization and impedance data which provide valuable insight into the relative magnitudes of the impedance contributions.

A typical cell developed in the present work consisted of the following five distinct layers: (a) porous Ni+YSZ anode support; (b) anode/electrolyte interlayer; (c) dense YSZ electrolyte; (d) cathode/electrolyte interlayer; (e) porous LSM ($LaSrMnO_3$) cathode current collector. The cell fabrication process is presented elsewhere [1]. Scanning electronic microscopic (SEM) analysis and voltammetry studies suggest that continuous films were generated and that completely hermetic seals were obtained.

Sample SOFC button cells prepared via the colloidal deposition approach were analyzed as a function of temperature and the results are displayed in Figure 1. The polarization curves clearly reflect a decrease in Area Specific Ohmic Resistance (ASOR) which is indicative of increasing temperature. However, Non-Linear Least Squares (NLLS) models of the polarization curves suggest that other many other factors also contribute to the improved performance [2]. Electrochemical Impedance Spectroscopy (EIS) was used to more clearly quantify these apparent factors. Figure 2 presents the impedance spectra of the five layer cell which shows two distinct semi-circles in addition to some apparent high frequency features. One can see that, with decreasing temperature, the high frequency intercept at Z' axis increases slightly, which could be attributed to a decrease in electrolyte conductivity. The charge-transfer reaction resistances (the diameter of the semi-circles) increase significantly with deceasing temperature. It should be pointed out that reaction

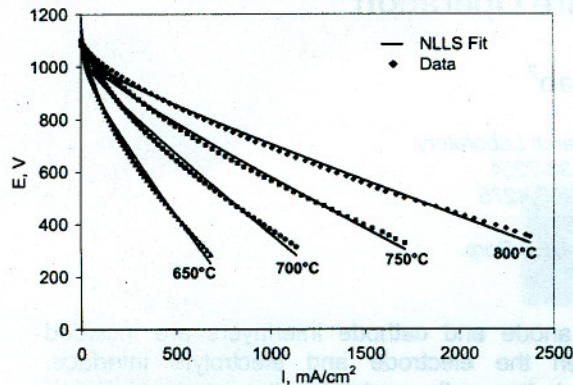resistance increased considerably when electrode interlayers were omitted.

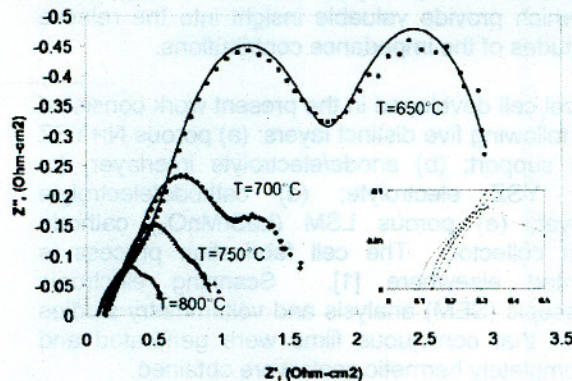Figure 1: Polarization curves of a single SOFC button cell as a function of temperature

Fig. 2. Impedance spectra taken at different temperatures for the SOFCs with thin electrolyte film (YSZ)

Impedance spectra data were modeled using an equivalent electrochemical circuit element approach assuming that each of the EIS spectra consisted of 3 semicircular features which overlapped slightly in the frequency domain (Figure 3). Because it was apparent that additional distributed elements were contained throughout each spectrum, Constant Phase Elements (CPE) were used in place of typical capacitor elements [3]. The regressed parameters obtained when the impedance spectra from temperature and polarization experiments was fit to the modified Randal's circuit was used to estimate the extent of cathodic, anodic, and ohmic resistances. These data are presented in Tables 1 and 2.
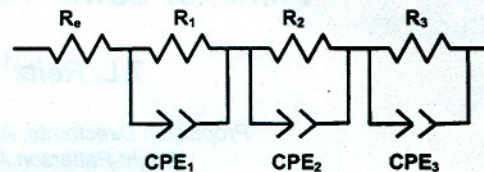
Re   Ohmic resistance
R_1:   High frequency semicircle resistance
CPE_1 High frequency semicircle constant phase element, $Z = 1/C(i \bullet \omega)^a$
R_2:   Mid-Range Frequency semicircle resistance
CPE_2: Mid-Range Frequency semicircle constant phase element
R_3:   Low Frequency semicircle resistance
CPE_3: Low Frequency semicircle constant phase element

Figure 3: Equivalent circuit of model fitting for impedance spectra obtained for single SOFC button cell (modified Randal's Circuit

Vs. Temp,	% of Total Resistance			
(°C)	IR	a	b	c
650	5.5%	8.0%	48.6%	37.9%
700	8.6%	10.4%	39.3%	41.7%
750	13.6%	7.9%	53.4%	25.1%
800	17.2%	8.9%	43.0%	30.9%

Table 1: Contribution of component real impedances for a 5-layer SOFC assembly as a function of Temperature at OCV

Vs. OCV,	% of Total Resistance			
(mV)	IR	a	b	c
0	17.2%	8.9%	43.0%	30.9%
100	21.6%	8.6%	46.1%	23.7%
200	24.6%	7.6%	49.5%	18.2%
300	25.8%	8.5%	49.0%	16.8%
400	25.2%	12.9%	45.4%	16.6%

Table 2: Contribution of component real impedances for a 5-layer SOFC assembly as a function of polarization at 800°C

Ohmic resistance of the button cells exhibited an Arrhenius dependence with temperature. However, the ohmic component did increase as a relative percentage of the total impedance of this cell as a function of temperature from a minimum of 5.5% at 650°C to a maximum contribution of 17.2% at 800°C (table 1). This trend is observed because the kinetic resistances, presumably contributions of the 1st and 3rd impedance features are significantly more temperature dependant than the ohmic losses. The

2

3rd semicircular feature, associated with cathodic processes, was observed to decrease in percentage of total impedance with temperature. The 1st and 2nd EIS features did not exhibit any clear trend within experimental uncertainty for the temperature experiments.

Polarization effects of 5-layer specimens

The effect of polarization was examined for typical button cell assemblies at 800°C and the results are shown in Figure 4. Good correlation of the data to the extended Randal circuit element was observed. The impedance parameters calculated using the described circuit models are presented in Table 3. The imaginary impedance components ($1/\omega C$) of the second and third features appear to decrease proportionately with polarization which is in stark contrast to their relative variation as a function of temperature described previously. The third feature was attributed to a cathodic process through experimentation and review of literature [4].
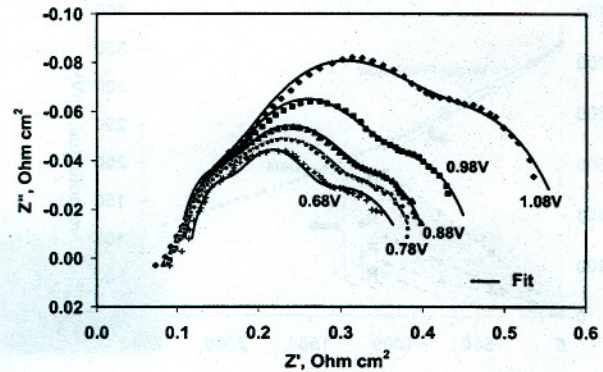

Figure 4: Impedance spectra obtained for single SOFC button cell (5-layer assembly) as a function of polarization at 800°C.

Bias vs. OCV	R_0 Ωcm^2	R_1 Ωcm^2	C_1 F/cm^2	α_1	R_2 Ωcm^2	C_2 F/cm^2	α_2	R_3 Ωcm^2	C_3 F/cm^2	α_3
0	0.10	0.052	0.0017	0.80	0.25	0.031	0.62	0.18	0.72	0.58
0.1	0.10	0.040	0.0002	0.95	0.21	0.024	0.64	0.11	0.86	0.61
0.2	0.10	0.031	0.0004	0.94	0.20	0.033	0.59	0.07	1.09	0.67
0.3	0.10	0.033	0.0005	0.92	0.19	0.040	0.57	0.07	1.29	0.70
0.4	0.11	0.051	0.0006	0.87	0.08	0.007	0.83	0.14	0.86	0.47

Table 3: Example impedance parameters calculated from model fitting for button cell SOFCs as a function of polarization at 800°C

Similar to the temperature experiments, EIS was used to deconvolute the relative impedances of the component processes. In each calculation, the individual real resistance term (R_0, R_1, R_2 or R_3) was determined via EIS and their relative contributions were calculated as a function of current density. The results of these models are plotted as a function of current density in Figure 5. Cathodic overpotentials (c) averaged 21.2% over the range of polarization. The cathodic contribution exhibited a decreasing trend with polarization which is consistent with the notion that the EIS semicircular 3rd feature is associated with electro-catalytic processes. The ohmic contribution was determined to be approximately 23% over the range of polarization values. While the magnitude of ohmic resistance was constant as a function of current density, its relative contribution increased illustrating the effect of high current densities on electrolyte conduction. The high frequency feature contributed approximately 9% of the total impendence as a function of polarization with no observable trend. It is assumed that this feature is associated with anodic reactions from previous experimentation, though this conclusion cannot be substantiated via this approach. The mid-range frequency feature represents the most significant contribution accounting for nearly 47% of the total impedance. The magnitude of the impedance increased linearly with current density suggesting that this feature is associated with charge transfer processes which could be either cathodic or anodic.
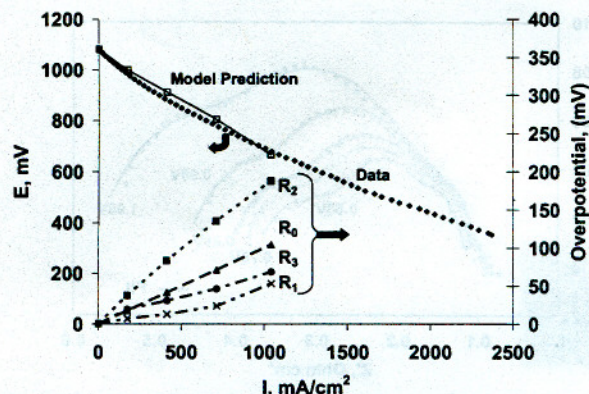
Figure 5: Polarization curve for single SOFC button cell (5-layer assembly) incorporating impedance model and specific contributions of individual spectral components at 800°C, (R_1) high-frequency contribution, (R_2) mid-range frequency contribution, (R_3) low-frequency contribution, (R_0) ohmic contribution.

Conclusion

Five-layer assemblies were evaluated as a function of temperature and polarization to understand the role of the thin film electrolytes and interlayers on power dense SOFCs. Ohmic resistances decreased with temperature consistent with that predicted from the Arrhenius law but exhibited no trend with polarization. Values of ohmic polarization were observed to be close to R0 obtained from EIS. EIS showed evidence of three distinct features which were attributed to different time-dependant processes within the fuel cell. Temperature appeared to impact each of these features to differing extents with a far greater dependence associated with the 3rd EIS semicircular feature relative to the high and mid-range frequency features. This observation is associated with a significant change in the double layer capacitance which was attributed to the cathode interface. Polarization experiments showed only modest variations in the features' relative impedances with increasing current density. These data appear to suggest that the 1st and 3rd semicircular features are

associated with kinetic processes while the real component of the 2nd feature is attributed to charge transfer resistance.

EIS data was used to deconvolute the relative contribution of these impedances. For thin film button cell assemblies, charge transfer resistance (2nd feature) appear to contribute most significantly to the overall impedance at OCV. Cathodic kinetic resistances also contributes significantly to the observed resistance, however, its relative significance decreases rapidly once the cell is polarized due to the enhanced driving force for reaction. Ohmic contributions are still rather considerable for these assemblies even though an electrolyte thickness of <10 μm was achieved. Contrary to results obtained for low temperature PEMFCs, anode contributions cannot be neglected under the conditions of this study [5-6]. EIS data suggest that as much as 12% of the total impedance can be associated with anode kinetics. As such, models which neglect these activation losses will tend to under-estimate Tafel coefficients providing unacceptable fits in the Tafel region.

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